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Title: Report on Current Assessment of Fabrication Routes to Large-Scale UN Production

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APPENDIX E

NTRD DOCUMENT COVER SHEET [1]

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Report on Current Assessment of Fabrication Routes to Large-Scale UN Production

Nuclear Technology Research and Development

Prepared for
U.S. Department of Energy
Advanced Fuels Campaign
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SUMMARY

Uranium mononitride has been proposed for nuclear fuels, given its favorable uranium atom density and thermal conductivity. Current synthesis routes are either cost prohibitive or leave behind unwanted carbon or oxygen contaminants. Here, a route known as oxidative ammonolysis is explored to convert uranium tetrafluoride to uranium dinitride. Reaction products have been examined and phases determined. The study here shows the possibility to convert uranium fluoride phases to uranium nitride phases.

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ACRONYMS

XRD X-ray Diffraction

UO_2 Uranium dioxide

UN Uranium mononitride

UF_4 Uranium tetrafluoride

UF_3 Uranium trifluoride

UN_2 Uranium dinitride

NH_3 Ammonia

ASSESSMENT OF FEEDSTOCK SYNTHESIS ROUTES FOR HIGH DENSITY FUELS

1. INTRODUCTION

There has been interest in the use of uranium nitrides as a nuclear fuel, in Gen IV reactors and as a way to improve neutron economics in current generation reactors. Uranium nitride (UN) possesses a higher uranium atom density than traditionally used uranium dioxide (UO_2) fuel. The higher uranium atom allows for a greater neutronic penalty from accident tolerant fuel claddings. Uranium nitride also has a higher thermal conductivity than UO_2, resulting in lower centerline temperatures within the fuel.

Conventional uranium nitride synthesis routes include carbothermic reduction of the oxide or hydriding and nitriding the metal. Both routes have their drawbacks, carbon and oxygen impurities for the former, and the need for high purity uranium metal in the latter. A synthetic route starting from uranium fluorides is explored here. Starting with UF_4 and heating under ammonia gas, a process known as oxidative ammonolysis, UN_2 can be made, at lower processing temperatures and starting with standard U-F bearing species utilized in industry at the front end of fuel fabrication lines. This could also by pass the oxidation of UF_6 and subsequent costly carbothermic reduction and nitridation steps that are currently proposed for UN fabrication at the commercial scale. UN2 can be readily decomposed to UN at elevated temperatures (1100 °C).

Here an experimental setup has been devised and four reactions have been performed. The reaction products have been analyzed for phases using XRD.

2. BACKGROUND

Current UN synthetic routes include hydriding and nitriding uranium metal and carbothermic reduction of the oxide. In the hydriding and nitriding route, high purity uranium metal is hydrided. The subsequent uranium hydride is then decomposed and nitrided in a purified nitrogen atmosphere. The resulting U_2N_3 is then decomposed to UN at high temperature [1]. The downside to the hydride/dehydride/nitride method is the cost associated with high purity uranium metal and the proliferation concerns associated with uranium metal. In the carbothermic reduction route, UO_2 is mixed with graphite powder and heated to reduce the oxide and form UC. The UC is then heated under a H_2-N_2 atmosphere to convert the UC to UN [2]. The drawbacks from the carbothermic reduction route include the vaporization of low vapor-pressure actinides and the inclusion of carbon impurities, as well as the high temperatures and long times involved.

A synthetic route using uranium fluorides and ammonia gas was published by Funk and Bohland, with UF_4 reacting with NH_3 at higher temperatures to form higher uranium nitrides [3]. The route was also used by Berthold and Hein and they proposed the intermediate phases of U(NH)F and $U(NH_2)F_2$ [4]. Yoshihara et al explored the reaction of UF_4 with Si and N_2 to obtain the sesquinitride (U_2N_3) [5]. More recently, Yeamans et al published an exploration of the oxidative ammonolysis of uranium fluorides [6]. The reaction of tetravalent ammonium uranium fluorides with an ammonia atmosphere at 800 °C was used to produce hexavalent UN_2, which was subsequently decomposed to UN. The reactions here were performed in quartz tubes, which are vulnerable to attack by the corrosive fluorine species produced in the reaction. This could lead to a source of oxygen and thus uranium oxide in the final product. The reaction was studied again showing the UN_2 product to have less than 1.0 wt. % UO_2 [7]. The route was further explored in Yeamans' [8] and Silva's [9] doctoral dissertations.

3. EXPERIMENTAL METHODS

3.1 Fluoride Conversion Process

The starting material used in the oxidative ammonolysis process was uranium tetrafluoride (UF_4), taken from LANL stock. The material had natural enrichment levels and was analyzed using XRD prior to the experimental instigations. The XRD is shown in Figure 1. The UF_4 starting material contained a small amount, on the order of 1 weight %, UO_2.

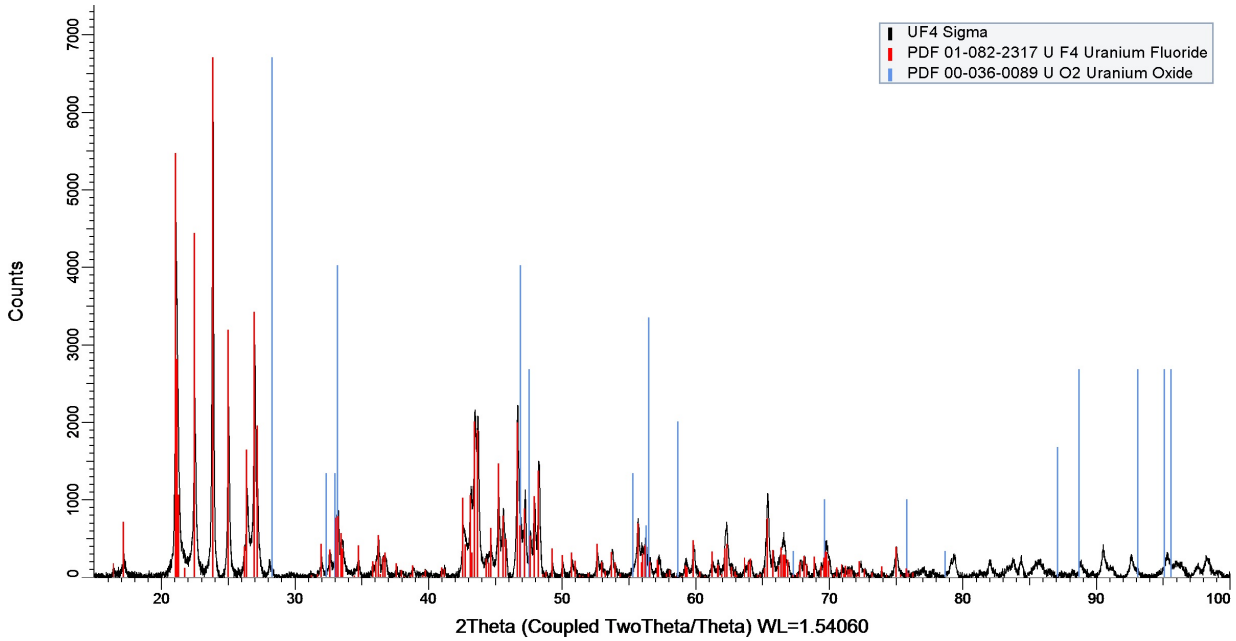

Figure 1. XRD pattern of UF_4 starting material, shown with lines from PDF database indicating UF_4 (red) and UO_2 (blue).

The experimental setup, shown in Figure 2, consisted of an Inconel 600 reaction vessel that could be sealed using valves on both ends. An Inconel sheathed Type K thermocouple was swaged into the reaction vessel to monitor the temperature of the reaction. The reaction vessel was placed in a clam shell furnace for heating in a chemical fume hood. The entire system up to the gas tank was evacuated to approximately 1 torr before every experiments. Ammonia gas was flowed during different segments of the experiment, as specified in Table 1, to determine optimal experimental parameters. The ammonia flow was set to maintain a pressure of approximately 500 torr (slightly sub-ambient). Approximately 1 gram of the UF_4 starting material was loaded into an Inconel 600 boat and sealed in the reaction vessel in an Ar atmosphere glovebox (<1 ppm O_2). Following the experiment, the reaction vessel was evacuated and sealed before being transferred to the Ar glovebox where the vessel was opened and the material removed for XRD analysis.

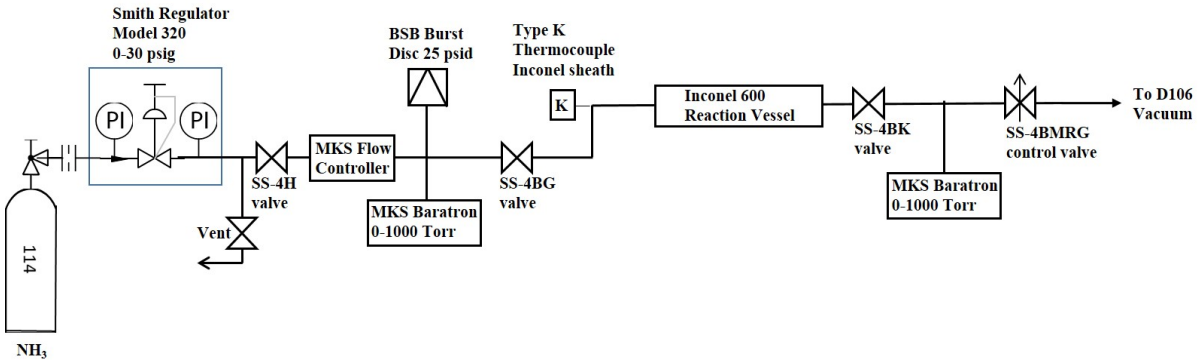

Figure 2. Manifold for the conversion of UF_4 to UN_2 using NH_3 (g). This set up was in a chemical fume hood.

Four reaction conditions were explored to investigate the conditions that produce the highest quantity of UN_2. The reaction temperature was varied from 890 to 1050 °C, time at temperature was set for a duration of 1 to 4 hours, and the ammonia gas was flowed at different segments for the experimental procedure (i.e. heating, at temperature, cooling). The four reaction conditions are shown in Table 1.

Experiment Number	Temperature	Ammonia Flow	Time at Temperature
1	1050 °C	At Temperature	1 hour
2	1050 °C	At Temperature, Cooling	2 hours
3	890 °C	Heating, At Temperature, Cooling	2 hours
4	890 °C	Heating, At Temperature, Cooling	4 hours

Table 1. Experimental Conditions used for oxidative ammonolysis.

3.2 X-Ray Diffraction

X-ray diffraction (XRD) was used to analyze the samples after the oxidative ammonolysis experiments. A Bruker XRD (D2 Phaser, Bruker AXS, Madison, WI, USA) was used for analysis. The material resulting from each test condition was ground and homogenized using a mortar and pestle in an Ar glove box. The powder was encapsulated using a low background, airtight specimen holder ring (A100B138-B141, Bruker AXS, Madison, WI, USA). Each sample was scanned over a two theta range of 14 to 98°, using a 0.02° step size and a 2 second dwell time.

4. RESULTS AND DISCUSSION

The oxidative ammonolysis conversion of UF_4 to UN_2 is proposed to have the overall following reaction:

$$UF_4 + 6NH_3(g) \rightarrow UN_2 + 4NH_4F(g) + H_{2(g)}$$

Not included in the balanced equation, are the possible intermediate species of U(NH)F and $U(NH_2)F_2$. It is also possible that the reaction occurs between the UF_4 decomposition products and the ammonia gas. The use of a residual gas analyzer may assist in shedding light on the reaction mechanism.

As discussed above, following the oxidative ammonolysis reaction, the reaction vessel was transferred to an Ar glovebox where the resulting powder was removed from the vessel and ground with a mortar and pestle for XRD analysis. The full pattern for all four runs and the starting UF_4 is shown in Figure 3.

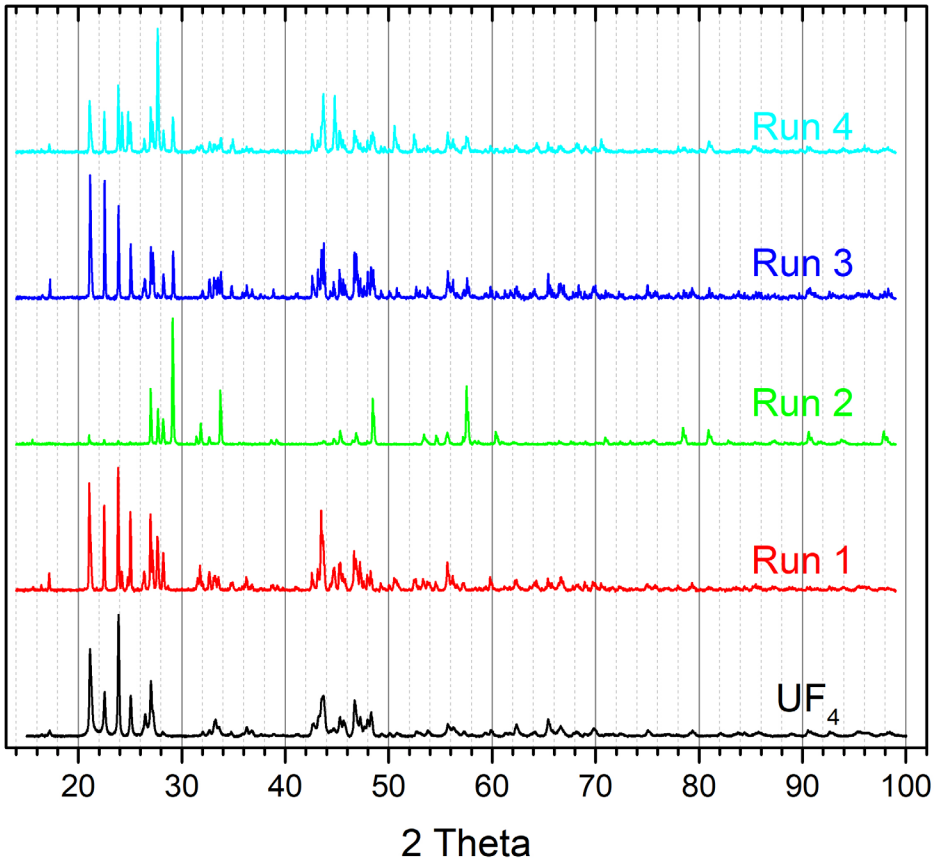

Figure 3. Diffraction patterns for the conversion of UF_4 to UN_2 for experiments 1-4 and the starting material UF_4.

The dominant phases seen in the diffraction patterns for the material following the conversion runs are UF_4, UF_3, UO_2, and UN_2. The UO_2 is also present in the UF_4 starting material. The UF_3 is a decomposition product of UF_4 that occurs at high temperatures. The UN_2 is the final product of the oxidative ammonolysis reaction. There are also present some unidentified peaks, believed to belong to intermediate species, such as U(NH)F and $U(NH_2)F_2$ [4]. Shown in Figure 4 are the diffraction patterns from 20 ° to 40 ° with peaks for UF_3, UO_2, and UN_2 labeled for clarity of these phases. The unlabeled peaks belong to either UF_4 (as can be compared to the starting material in the bottom most pattern) or an unidentified intermediate phase.

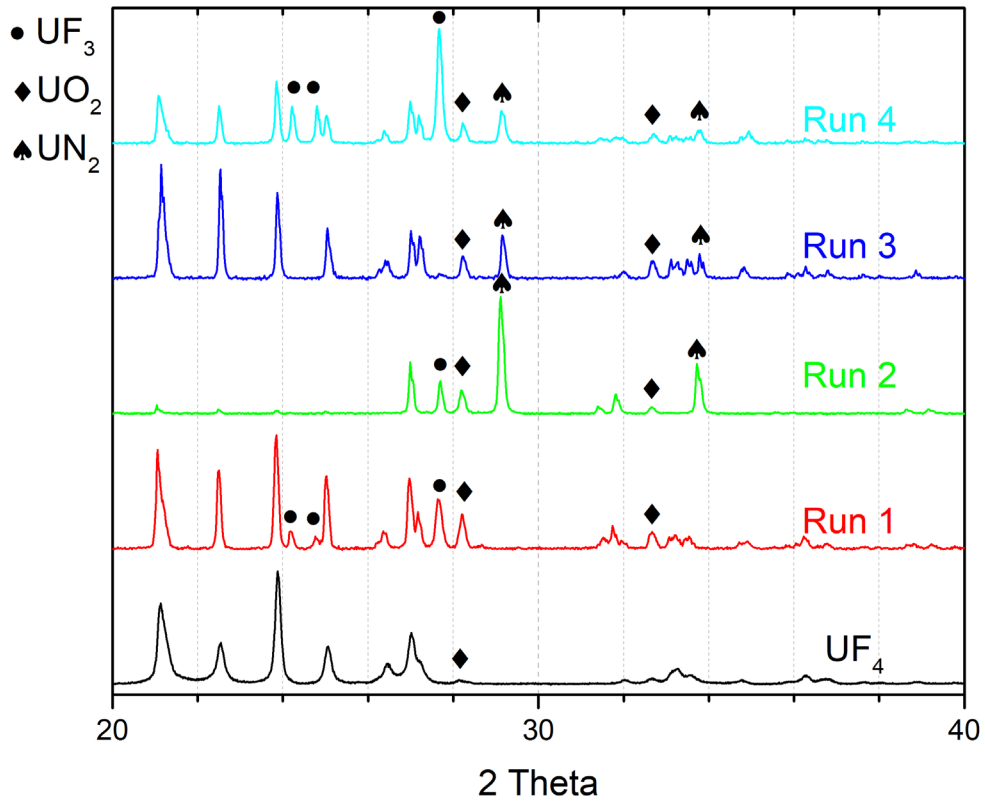

Figure 4. Enlarged region of the diffraction patterns with labeled peaks.

From the diffraction patterns, it is evident that Run 1 did not produce any UN_2, but did increase the level of UO_2 present and formed some UF_3 from UF_4 decomposition. The lack of UN_2 in the final product from Run 1 is most likely due to not being exposed to the ammonia atmosphere for a long enough period of time, especially upon cooling. Run 2 was the most successful conversion, with the prominent phase present as UN_2. The small UF_4 peaks indicate the reaction consumed the majority of the starting material. The presence of UF_3 and possible intermediate phases indicate that the reaction did not go all the way to completion, suggesting longer time may be needed. The diffraction pattern from Run 3 contains peaks belonging to UF_4, UO_2, and UN_2, indicating an incomplete reaction. Run 4 has all phases present. The difference between Run 3 and Run 4 is a longer period at temperature. The increase in UF_3 peaks and decrease in UF_4 peaks indicate that a longer time at temperature leads to an increase in the decomposition of UF_4, regardless of the flowing ammonia gas. When looking at all four runs it is clear that flowing ammonia is necessary upon cooling the reaction vessel. This suggests that the primary reaction may take place between a decomposition product of UF_4 and ammonia. The apparent completion of the reaction and lack of starting material leftover in Run 2 suggest that the higher temperature is more favorable, compared to Runs 3 and 4.

5. CONCLUSIONS AND FUTURE WORK

An experimental setup was constructed that would allow for the conversion of UF_4 to UN_2 while controlling the atmosphere and temperature. The reaction vessel and reaction boat were constructed out of Inconel 600 to limit corrosion and possible oxygen sources. Four reactions were performed varying the temperature, time at temperature, and flow of ammonia. The reaction material was then analyzed using XRD for the phases present. It is evident that the flow of ammonia is necessary at least at temperature and during cooling. It also appears that a higher temperature is more favorable for conversion to UN_2.

Future work includes repeating Run 2 and optimizing the reaction parameters to maximize the yield of the reaction. Work will also be done using a residual gas analyzer to determine what gases are evolved and during what part of the reaction. The next step in the process would be to take the high yield UN_2 material and convert it to UN. To further minimize oxide impurities, the starting UF_4 material could be cleaned of oxides impurities. This could possibly be done using ammonium bifluoride, which reacts with UO_2 to form ammonium uranium fluorides.

While this reaction has not yet been optimized, this is a viable route to uranium nitride. The synthesis does not include the introduction of carbon into the system, and thus carbon impurities in the final product. This reaction is also performed at temperatures significantly lower than carbothermic reduction (1000 °C compared to 1800 °C). The reaction also uses UF_4 as a starting material, which is found in the commercial processing of uranium and does not need accrue the expense and proliferation concerns of uranium metal.

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